THE LIBERATION OF FORMALDEHYDE THROUGH THE AGENCY OF CALCIUM CARBIDE.

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DURING the last two years a very considerable amount of work has been done at the Maine Laboratory of Hygiene upon the matter of formaldehyde disinfection. In the course of this work the formalin-permanganate method was first worked out as a means of practical disinfection. In one way this method seemed an anomaly, in that part of the agent which was to do the work of disinfection was itself used up in the reaction that furnished the heat to evaporate the formaldehyde solution. In looking for a means of surmounting this difficulty, the use of calcium carbide was suggested, and the subsequent work with this compound forms the basis of this paper.

As is well known, when calcium carbide and water are mixed, there results a violent reaction from which acetylene gas is formed and driven off, while calcium oxide is theoretically the product remaining in the generator. In actual practice the residue in the generator is calcium hydroxide, resulting from the union of the first-formed oxide with water. The value of this reaction for disinfection does not lie in the products formed, but in the heat which results from the reaction. It was purposed to use this heat to evaporate the formaldehyde that was to be added to the calcium carbide, just as in the formalin-permanganate method the heat resulting from the oxidation of a portion of the formaldehyde was employed to evaporate the unoxidized portion. In this case it seemed probable that there would not be the destruction of formaldehyde noted in the other method.

In the work ordinary commercial calcium carbide and formaldehyde solution were used. The particular lot of formaldehyde solution used assayed 35.27 per cent by weight of formaldehyde. These reagents were used, as it was desired to get only such results as would be obtained in actual disinfection by this method, if it turned out to be of any value.

The first work necessary was to determine the proportions of the reagents to be used. In this work it was first noted that when the

formaldehyde was added to the calcium carbide, the formaldehyde being in its original strength, there was practically no reaction. In other words there did not seem to be enough water to react with carbide in the formalin solution alone. By using enough carbide to leave a thoroughly dry residue in the generator it was found that the formalin solution should be diluted by its own volume of water in order to give the best results. Starting then with a solution half water and half formalin, a large number of tests were made to determine the amount of carbide necessary to give a dry residue in the generator and at the same time leaving as little as possible of the carbide unused. It was finally decided to use six grams of the carbide to every 10 c.c. of the diluted formaldehyde solution. Experiments in using the large amounts of the reagents in the disinfecting-room gave as satisfactory results with these proportions as did the smaller amounts in preliminary experiments.

The work done in determining the proper proportions of the reagents showed that the best results were to be obtained when the carbide was in size about that of a pea. If in a powdered form the reaction was too violent, and if much larger than a pea the reaction was so slow as to produce an insufficient amount of heat to evaporate the formaldehyde. At the same time it was noted that a rather low dish, with walls about eight or ten inches high, and with a very wide bottom was preferable for a generator. The reagents and generator being as above described, the reaction, which starts rather slowly, is over in between six and seven minutes.

To determine the amount of formaldehyde liberated by this reaction, air was drawn from the room in which disinfection was going on. The apparatus used for this purpose was the one formerly used in determining the formaldehyde in rooms charged by the formalin-permanganate method, fully described in the paper on that work in the *Fourteenth Report of the Maine Board of Health.* In brief the apparatus was this:

A glass tube was passed through a hole in the door of the disinfecting-room so as to project about three feet into the room, the end in the disinfecting-room terminating in a funnel. The end of this glass tube, which was outside the disinfecting-room, was connected to the first of a series of three Dreschsel gas bottles, each containing 75 c.c. of distilled water. The last of the series of Dreschsel bottles was connected with a 10-liter bottle, filled to the 10-liter mark with water, any amount of which

could be siphoned off at pleasure. All rubber connections were sealed with paraffin wax and thoroughly tested to see that they were air-tight. The stoppers of the several bottles were also sealed in with paraffin wax.

In practice 20 minutes were allowed to elapse after the reaction was over before the siphon was started, so that there might be time for the gas to diffuse uniformly throughout the room. The apparatus was then allowed to run at such a rate that at least 35 minutes were required to draw 10 liters of air through the Dreschsel bottles. The pressure conditions were then equalized and the gas bottles were disconnected, their contents were poured into a 500 c.c. flask, each bottle washed three times with distilled water, and the washings added to the contents of the 500 c.c. flask. To the contents of the flask were now added 10 c.c. of a solution of standard potassium cyanide; the flask was well shaken, allowed to stand for five minutes, then 10 c.c of a solution of N-10 silver nitrate, previously acidified with 10 drops of 75 per cent c.p. nitric acid, added; the whole made up to 500 c.c.; mixed; 100 c.c. filtered, and the excess of silver in the filtrate determined by Volhard's method. From this the amount of formaldehyde in the 10 liters of air examined was calculated, and, knowing the cubic contents of the room and the amount of formaldehyde introduced, the percentage of the original amount of formaldehyde that was yielded by the reaction was easily calculated. On three different tests the amount of formaldehyde found in the room ranged from 6.12 per cent to 11.4 per cent.

When the room was opened at the end of four hours the odor of formaldehyde was not so strong as to cause any annoyance to either the eyes or to the throat, even when the formaldehyde was used in the proportions of 500 c.c. to 1,000 cubic feet. In fact there was not so much trouble to be experienced in entering the room thus charged as there was in entering the same room when charged by the formalin-permanganate method with 200 c.c. to 1,000 cubic feet. Neither was the odor of acetylene very strong. It cannot be expected that all of this loss of formaldehyde is to be accounted for by leakage, as this did not happen when simply formaldehyde was evaporated into the room. It is possible that the mixture of the two gases—acetylene and formaldehyde—may diffuse more rapidly than formaldehyde alone, as a stronger odor of acetylene was always to be noted outside of the disinfecting-room than was ever the odor of formaldehyde, when this alone was used in charging.

Just before the completion of the reaction, when the effervescence was at its height, a yellowish-brown scum began to form over the entire surface of the liquid, and this rapidly thickened, so that in a short time the gas seemed to have difficulty in forcing its way through the scum. This scum seemed to increase in amount from the time of its appearance until the end of the reaction. No chemical examination was made of this scum, as the object of the work was to deter-

mine the bacterial efficiency of the method rather than to determine the chemical products formed. It is possible that the aldehyde, in the presence of the hot alkali, formed some solid condensation product, as aldehydes often do under these conditions. This would of course cause a considerable loss of formaldehyde for disinfecting purposes. At any rate the yield of formaldehyde by this process is very low, and the bacterial results reflect this condition.

The bacterial work was done in a room having a capacity of 862 cubic feet, measuring 20×4 ½×10 feet high, and containing a small jog at one end. The room had one door measuring 3×7 feet, and two windows. One was on the outside of the building, measuring 3 ¼×6 ¼ feet, and the other opened into another room. This window was 8 feet from the floor, and measured 1×9 ½ feet. No attempts were made to make the door or windows air-tight, they being left in their natural condition so as to have disinfecting conditions as near those actually encountered by the health officer. The interior of this room was papered. The technique of the bacterial work was as follows:

A piece of heavy glazed paper was bent so as to form a shelf. Then five strips of filter paper were inoculated by loops of broth or heavy smears of blood-serum cultures of the organisms to be used. Each strip was picked up with sterile forceps, and, with sterile shears, cut into two pieces. One piece was put on the shelf of glazed paper, and the other dropped into a tube of bouillon as a control. Five strips, inoculated with the same organism, were put on each paper shelf, and the latter then placed in the disinfecting-room. Here the paper shelves were distributed in all parts of the room, and also at all heights from the floor to the ceiling. When the requisite number of cultures were in position the reagents were mixed and the room closed for four hours. At the end of this time each paper shelf was removed from the room; the pieces of infected filter-paper picked up with sterile forceps; introduced into separate tubes of sterile bouillon, and incubated at 37.5° C. for 196 hours, at the end of which time they were examined. All growths were examined microscopically to see if they were those put upon the paper or were the result of contamination of some sort.

In the work with the formalin-permanganate method the proportions of 200 c.c. to 1,000 cubic feet gave very satisfactory results and work was started using these proportions. The cultures used were colon, diphtheria, pneumococci, pyocyaneus, albus, tetragenus, typhoid, prodigiosus, and mixed cultures from throat swabbings. The whole number of cultures exposed here was 335. The work was done on three separate days, the temperatures being respectively 73°, 74°, 74° F. The average increase in the humidity in the test-room was 11.3 per cent.

TABLE 1.

DISINFECTION TEST, 200 C.C. TO 1,000 CUBIC FEET.

Culture	Number	Growth	No Growth
Colon	35	1	34
Diphtheria	30	7	23
Pneumococci	35	4	31
Pyocyaneus	40	20	20
Albus	45	13	32
Tetragenus	30	2	28
Typhoid	25	2	23
Prodigiosus	30	9	21
"Mixed"	65	20	45
Total	335	78	257

These proportions not giving satisfactory results the amount of formaldehyde was raised to 300 c.c. to 1,000 cubic feet. Here again work was spread over three separate days, their respective temperatures being 79°, 81°, and 70° F., and the average rise in humidity in the test-room was 11.8 per cent. Three hundred and forty-nine cultures were exposed; 168 of these were buried cultures. The results follow.

TABLE 2.

DISINFECTION TEST, 200 C.C. TO 1,000 CUBIC FEET.

Culture	Number	Growth	No Growth
Pneumococci	25	2	23
Pyocyaneus	48	4	44
Albus	53	0	53
Streptococci	9	0	9
Typhoid	48	4	44
Prodigiosus	23	2	21
Colon	25	1	24
Tetragenus	16	2	14
Diphtheria	31	19	12
Aureus	20	19	1
Throat	26	2	24
"Mixed"	25	19	6
Total	349	74	275

The results being again unsatisfactory the proportions were raised to 500 c.c. to 1,000 cubic feet. The work was done on three separate days, the temperatures being 74°, 79°, and 76° F. The average increase in the humidity was 13.2 per cent. In all, 268 cultures were exposed of which 120 were buried and 148 were open cultures. The method of burying the cultures was that used in my work on the formalin-permanganate method, and there fully described. In brief it was as follows:

A piece of tin six inches square had a circular hole cut in the center. Over this were spread the requisite number of thicknesses of whatever kind of cloth was used—

silk, cotton-flannel, or ticking. On the upper layer of the cloth were placed five inoculated slips of filter-paper, so as to be over the circular hole. On top of these was spread the same number of cloths as were below, the whole being capped by duplicate of the tin bottom, and then the edges were clamped tight so that the only way for the gas to reach the organisms was by penetrating the layers of cloth exposed by the holes in the tin.

TABLE 3.

DISINFECTION TEST, 500 C.C. TO 1,000 CUBIC FEET.

Culture	Number	Growth	No Growth
Colon	30	0	30
Diphtheria	40	0	40
Pheumococci	30	0	30
Pyocyaneus	20	0	20
Albus	13	0	13
Typhoid	63	0	63
Subtilis	22	5	17
Anthrax	30	0	30
"Mixed"	20	0	20
Total	268	5	263

From these results it seems that it is possible to get efficient disinfection by this method provided that use is made of not less than 500 c.c. of formaldehyde solution for every 1,000 cubic feet of room space to be disinfected. The method does not compare favorably with the formalin-permanganate method, it requiring twice the amount of formaldehyde for efficient disinfection that the latter does. With the proportions used by me there was not such an increase in the humidity of the test-room as there was with the permanganate method. It may be that under some conditions this method may be of use. The acetylene and formaldehyde gases had no more effect on flies and mosquitoes than does formaldehyde gas alone.

TABLE 4.

SUMMARY

	Growth	No Growth	Total
500 c.c.	5	263	268
300 c.c.	74	275	349
200 c.c.	78	257	335
Total	157	795	952